Photoinduced Molecular Transformations. Part 109.[1] Conformational Dependence of the Stereochemistry of Photochemical 1,3-Acyl Shifts of β,γ-Unsaturated Cyclic Ketones: Conformation-specific Photorearrangements of Steroidal β,γ-Unsaturated Cyclic Ketones, 7a-Homocholest-5-en-7a-one and 4a-Homo-5α-cholest-1-en-4-one†‡

Hiroshi Suginome,* Toshiharu Ohtsuka, Yoshimasa Yamamoto, and Kazuhiko Orito
Organic Synthesis Division, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan
Carlos Jaime§ and Eiji Ōsawa
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Direct irradiation of 7a-homocholest-5-en-7a-one in t-butyl alcohol with Pyrex-filtered light resulted in photorearrangement to 5-vinyl-7-nor-5α-cholestan-6-one and 5,7-cyclo-7a-homo-5α-cholestan-7a-one *via* 1,3-acyl and oxa-di-π-methane rearrangements. Sensitization and quenching studies indicated that the former product arose from an excited singlet state of the β,γ-unsaturated ketone while the latter arose from an excited triplet state.

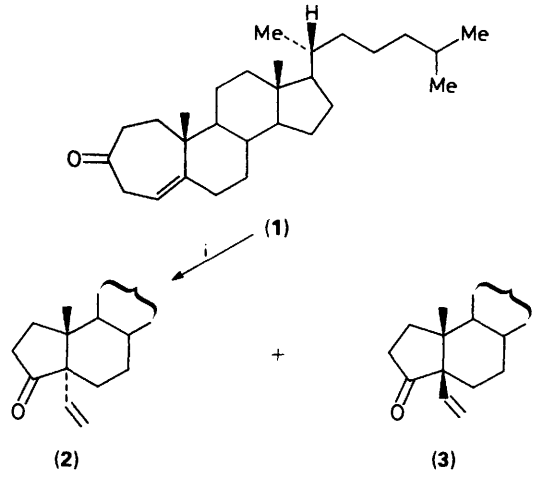
Direct irradiation of 4a-homo-5α-cholest-1-en-4-one in t-butyl alcohol with Pyrex-filtered light, however, gave 1β-vinyl-4-nor-5α-cholestan-2-one arising from a [1,3] acyl shift as the only product without any accompanying product arising from the oxa-di-π-methane rearrangement. The populations of boat and chair conformations of the ground state of the above β,γ-unsaturated ketones and several related A-ring ketones were calculated by the empirical force field method. The stereochemistry of the products of 1,3-acyl shift in the present photorearrangements, 5-vinyl-7-nor-5α-cholestan-6-one and 1β-vinyl-4-nor-5α-cholestan-2-one, was found to depend clearly upon the conformation of the ground state of the starting β,γ-unsaturated steroidal ketones and the ratio of the stereoisomers of the products was found to depend on the ground-state population of the conformers of the starting unsaturated ketones.

Since the first observation of the photochemical rearrangement of bicyclo[3.1.0]heptenones,[2] extensive investigations have been carried out on the photorearrangements of β,γ-unsaturated carbonyl compounds over the past two decades.[3,4] Direct irradiation of β,γ-unsaturated ketones thus results mostly in [1,3] acyl migrations to give isomeric β,γ-unsaturated ketones. Triplet sensitization, on the other hand, results in the [1,2] acyl migrations (the oxa-di-π-methane rearrangement) to give isomeric cyclopropyl ketones.

Extensive mechanistic studies[3] have indicated that the [1,3] acyl migrations take place from either the n,π* singlet (S_1) or triplet (T_2) states while the [1,2] acyl migrations take place from the π,π* triplet (T_1) states. Although most β,γ-enones undergo only the [1,3] acyl shift on direct photolysis, some β,γ-enones, in which intersystem crossing from the singlet to the triplet state is more efficient, gave products arising from both [1,2] and [1,3] acyl shifts.

Investigations with regard to the stereospecificity of the migration[4] and CIDNP studies[5] have indicated that the photorearrangement proceeds either by a concerted mechanism or through a tight biradical pair.

Among the numerous acyclic and cyclic substrates used for the investigation of the photorearrangement of β,γ-unsaturated carbonyl compounds, steroidal β,γ-unsaturated cyclic ketones have occupied a unique position for the investigation of the stereochemistry of this photorearrangement.[4e,d,f,h,j] For example, Seeman and Ziffer[4j] investigated the photorearrangements of 4a-homocholest-4a-en-3-one (**1**) and found that direct irradiation resulted in the formation of 5-vinyl-4-nor-5α-cholest-5-en-3-one (**2**) and the 5β-epimer (**3**) in a ratio of 1:4.8 arising from the [1,3] acyl shift (Scheme 1) and the sensitized irradiation of both vinyl ketones (**2**) and (**3**) led to a single cyclopropyl ketone which arose from the oxa-di-π-methane rearrangement.[4j]



Scheme 1.

† Part of this work was presented at the symposium on photochemistry (Thukuba, Japan), 18th October 1983, by H. Suginome and T. Ohtsuka, Abstr., p. 165.

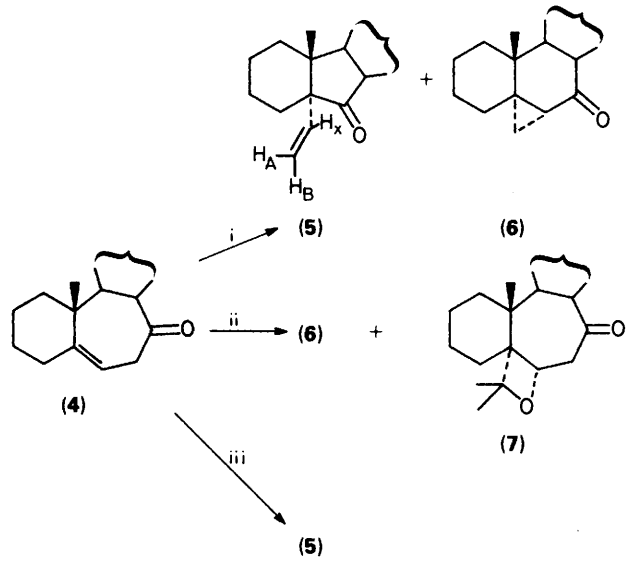
‡ Nomenclature according to 1989 I.U.P.A.C. recommendations: *Pure Appl. Chem.*, 1989, **61**, 1783.

§ *Present address:* Department de Quimica, Facultat de Ciencies, Universitat Autonoma de Barcelona, 08193 Ballaterra, Spain.

From the viewpoint of synthesis, these photochemical ring contractions are of utility and we were interested in the factors which determined the stereochemistry of the resulting two vinyl ketones (**2**) and (**3**) in the photorearrangement of the 7-membered β,γ-unsaturated cyclic ketone (**1**) where the double bond is located within the ring. In this paper we report (*a*) the results of our study of the photorearrangement of the two steroidal β,γ-unsaturated ketones, 7a-homocholest-5-en-7a-one (**4**)[4j] and 4a-homo-5α-cholest-1-en-4-one (**7**),[4j] and (*b*) the results of empirical force-field calculations on the populations of the predominant ground-state conformers of the 4a-homocholest-4a-en-3-one (**1**) studied by German[4h] and American authors,[4j] 7a-homocholestenone (**4**),[6] 4a-homocholestenone (**11**),[7] and all the possible related 4a-homocholestenones (**13**), (**14**), and (**15**). The stereochemistry of the products which arose from the [1,3] acyl shift in the photo rearrangements of these homocholestenones has been found to be correlated with the population of their ground-state conformation.

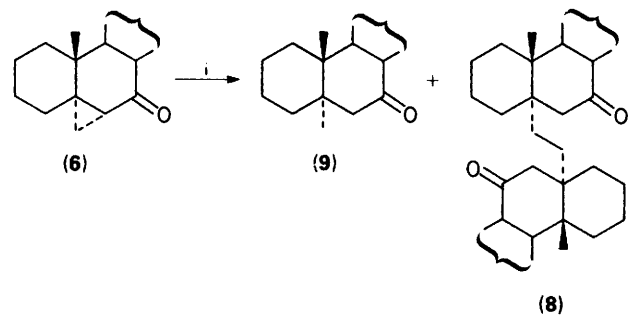
Results

Direct Irradiation of 7a-*Homocholest-5-en-*7a-*one* (**4**) *in t-Butyl alcohol* (*Scheme* 2).—The UV spectrum of the β,γ-unsaturated ketone (**4**)[6] in t-butyl alcohol exhibited an absorption maximum at 275 mm (ε 225) assignable to the n ⟶ π* transition. The photoreaction of the β,γ-unsaturated ketone (**4**) in t-butyl alcohol with a 100 W high-pressure Hg arc through a Pyrex filter for 17 h in an atmosphere of nitrogen gave two crystalline products (**5**) and (**6**) in 30 and 33% yields. Mass spectrometry and elemental analyses established that the two products had the same molecular formula $C_{28}H_{46}O$. The IR spectrum of the photoproduct (**5**) exhibited a band at 1 730 cm^{-1} ascribable to the 5-membered cyclic ketone. The ^1H NMR spectrum of the photoproduct (**5**) exhibited a series of signals assignable to a vinyl group (see Experimental section). These spectral results suggested that the photoproduct (**5**) is 5-vinyl-7-norcholestan-6-one, arising from a 1,3-acyl shift. The configuration of the 5-vinyl group in the product (**5**) was established as α by nuclear Overhauser enhancement (NOE) measurements. Thus, no enhancement of the vinyl proton signals was observed when the 19-H signal was irradiated.

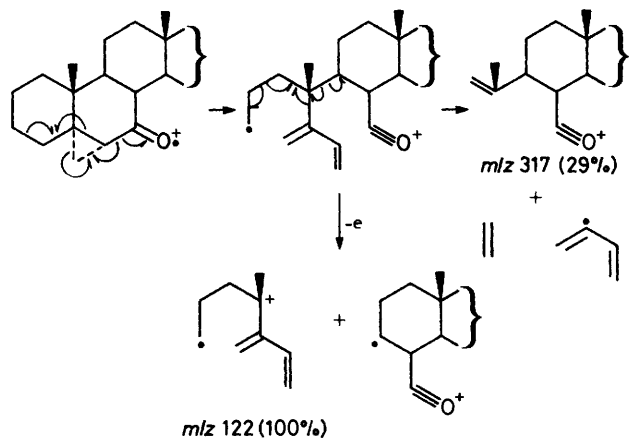


Scheme 2. *Conditions:* i, *hν*, Bu^{t}OH; ii, *hν*, acetone; iii, *hν*, Bu^{t}OH, piperylene.

The IR spectrum of the photoproduct (**6**) exhibited a band at 1 668 cm^{-1} ascribable to the 6-membered cyclic ketone conjugated with a cyclopropyl group. The ^1H NMR spectrum included a signal at δ 0.55 assignable to the cyclopropane proton. These spectral results suggested that the product (**6**) was 5,7-cyclo-7a-homocholestan-7a-one (**6**) arising from the oxa-di-π-methane rearrangement of the β,γ-unsaturated ketone. In agreement with this assignment, reduction of the photoproduct (**6**) with lithium in liquid ammonia gave major and minor products (**9**) (83%) and (**8**) (3%) (Scheme 3). The molecular formula of the major product, $C_{28}H_{48}O$, was confirmed by means of high resolution mass spectrometry. The IR spectrum exhibited an unstrained carbonyl absorption at 1 717 cm^{-1}. The ^1H NMR spectrum showed three 3 H singlets ascribable to the three Me groups attached to tertiary carbon atoms. These spectral results, together with the ORD measurements, which exhibited a negative Cotton effect,[8] indicated that the product was 5-methyl-5α-cholestan-7-one (**9**). The mass spectrum of the product (**6**) exhibited the base peak at *m/z* 122 and a significant peak at *m/z* 317, the probable genesis of which is outlined in Scheme 4.

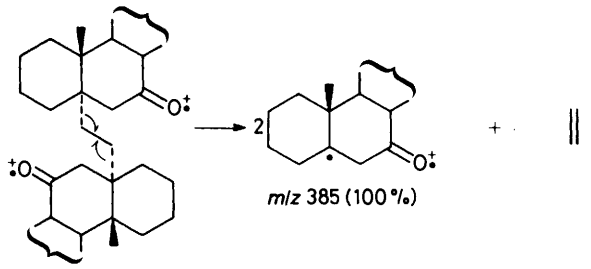


Scheme 3. *Reagent:* i, Li–liq. NH_3.



Scheme 4. Mass spectral fragmentation of (**6**).

The high resolution mass spectrum of product (**8**) indicated that it has the molecular formula $C_{56}H_{94}O_2$. The IR spectrum included a band at 1 716 cm^{-1} attributable to an unstrained carbonyl function. The ^1H NMR spectrum exhibited 6 H, 3 H, and 3 H singlets at δ 0.64, 1.23, and 1.25 respectively. These results, together with the mass spectral fragmentation (*vide infra*), indicated that the structure is the dimer (**8**) of 5-methyl-5α-cholestan-7-one. The above three singlets are ascribable to overlapping 18- and 18′-H, 19- and 19′-H of the dimer. 19- and 19′-H appear as separated singlets owing to hindered rotation of



Scheme 5. Mass spectral fragmentation of (**8**).

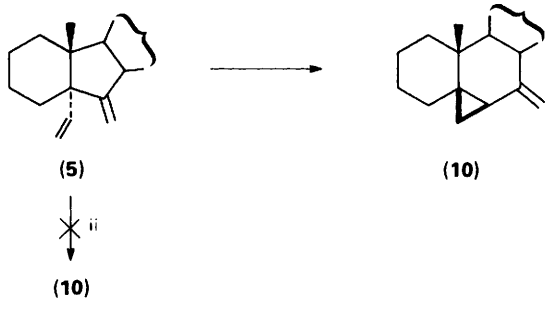
the dimethylene bridge. The mass spectrum included the base peak at *m/z* 385, the genesis and structure of which are outlined in Scheme 5.

Sensitized Irradiation of 7a-*Homocholest-5-en-*7a-*one* (**4**) *in Acetone* (*Scheme* 2).—The sensitized photolysis of 7a-homocholest-5-en-7a-one (**4**) in acetone for 16 h gave the cyclopropyl ketone (**6**) in 25% yield together with the product (**7**) in 17% yield. As expected, the vinyl ketone (**5**) arising from a 1,3-acyl shift was also found. The spectral data for the product (**7**) are consistent with it being a cycloadduct arising from a Paterno–Büchi reaction of acetone with 7a-homocholestenone (**4**) (see Experimental section) although the assigned stereochemistry was only tentative.

These sensitization studies indicated that the cyclopropyl ketone (**6**) is the product arising from an excited triplet state of 7a-homocholestenone (**4**).

Photolysis of 7a-*Homocholest-5-en-*7a-*one* (**4**) *in t-Butyl Alcohol in the Presence of a Triplet Quencher* (*Scheme* 2).—The photolyses of the β,γ-unsaturated ketone (**4**) in t-butyl alcohol containing piperylene as a triplet quencher for 18 h gave solely the vinyl ketone (**5**) in 56% yield without any accompanying cyclopropyl ketone (**6**). A Stern–Volmer plot for this reaction is shown in Figure 1. Φ_0/Φ increases linearly with the concentration of piperylene. The quantum yields, Φ, of the vinyl ketone (**5**) and the cyclopropyl ketone (**6**) in the photolysis of the β,γ-unsaturated ketone (**4**) in the absence of the quencher were 0.14 and 0.11. The plot in Figure 1 indicated that the cyclopropyl ketone (**6**) is formed exclusively from an excited triplet state.

The Oxa-di-π-methane Rearrangement of 5-*Vinyl-*7-*nor-*5α-*cholestan-*6-*one* (*Scheme* 6).—The oxa-di-π-methane rearrangement of a β,γ-unsaturated ketone to a cyclopropyl ketone has been reported for a variety of compounds.[3] The stereospecificity of the rearrangement has also been demonstrated in a steroidal substrate.[4j] The photolysis of the β,γ-unsaturated ketone (**5**) in acetone with a 100 W high-pressure Hg arc gave a crystalline product (**10**) in 52% yield. High-resolution mass spectrometry indicated the molecular formula to be $C_{28}H_{46}O$. The IR and



Scheme 6. *Conditions:* i, *hν*, acetone; ii, *hν*, Bu^{t}OH.

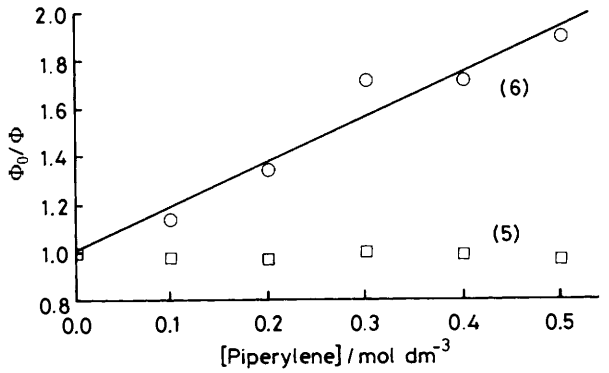
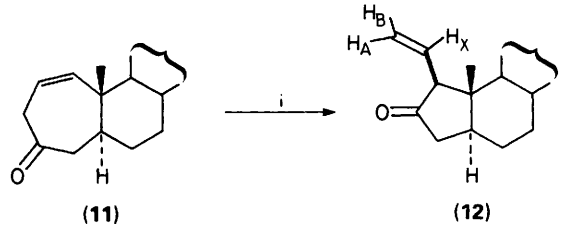


Figure 1. Stern–Volmer plot for the formation of 5,7-cyclo-7a-homo-5α-cholestan-7a-one (**6**) and 5-vinyl-7-norcholestan-6-one (**5**) by irradiation of 7a-homocholest-5-en-7a-one (**4**) in t-butyl alcohol.

mass spectra were consistent with those of the expected 5,7-cyclo-7a-homo-5β-cholestan-7a-one (**10**), which is isomeric with the photoproduct (**6**).

Photolysis of the unsaturated ketone (**5**) in t-butyl alcohol in the absence of a sensitizer for 15 h resulted in recovery of the starting material and irradiation for 43 h led to the formation of a complex mixture. This selectivity of the oxa-di-π-methane rearrangement of the vinyl ketone (**5**) is entirely analogous to the reported stereospecificity of the oxa-di-π-methane rearrangements of 5-vinyl-4-nor-5α- and -5β-cholestan-3-ones.[4j]

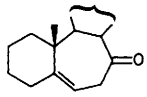
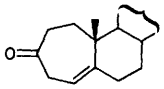
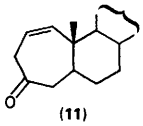
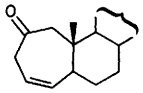
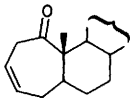
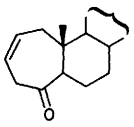
Direct Irradiation of 4a-*Homo-*5α-*cholest-*1-*en-*4-*one* (**11**)[7] *in t-Butyl Alcohol* (*Scheme* 7).—The UV spectrum of the β,γ-unsaturated ketone (**11**) in t-butyl alcohol exhibited an absorption maximum at 282 nm (ε 55) assignable to the n ⟶ π* transition. Photolysis of the ketone (**11**) in t-butyl alcohol with a 450 W high-pressure Hg arc through a Pyrex filter for 3.5 h in an atmosphere of nitrogen gave the major product (**12**) (34%) together with several minor products. The molecular formula of the product (**12**) was confirmed to be $C_{28}H_{46}O$ by means of FI high resolution mass spectrometry. The IR spectrum showed a band at 1 746 cm^{-1} ascribable to the 5-membered cyclic ketone. The ^{1}H NMR spectrum included a series of signals attributable to a vinyl group (see Experimental section). These spectral results suggested that the product is 1-vinyl-4-nor-5α-cholestan-2-one arising from a 1,3-acyl shift. The configuration of the vinyl group was proved to be β by means of NOE measurements; irradiation of the signal due to 19-H resulted in an enhancement of the vinyl proton signals. The 1α-epimer of the vinyl-4-norcholestanone (**12**) or the cyclopropyl ketone arising from the excited triplet state was not found.



Scheme 7. *Conditions:* i, *hν*, Bu^{t}OH.

Conformer Populations of All Possible β,γ-4a-*Homocholestenones and* 7a-*Homocholest-5-en-*7a-*one calculated by Means of an Empirical Force-field Method and the Conformational Dependence of the Stereochemistry of the Photorearrangements of the* β,γ-*Unsaturated Ketones.*—It has thus been established that in contrast to the photorearrangement of 4a-homocholest-4a-en-4-one (**1**), direct irradiation of 7a-homocholest-5-en-7a-

Table. Steric energies and conformer populations of 7a-homocholest-5-en-7a-one (**4**) and five 4a-homocholestenones as calculated by MM2.[a]

Structure[b]	Conformations of 7-membered ring	Steric energy/ kcal mol^{-1}	Population (%)
 (4)	Boat		99.98[c]
	Chair		0.02[c]
 (1)	Boat	53.37	30.77
	Chair	52.89	69.23
 (11)	Boat	55.61	0.77
	Chair	52.73	99.23
 (13)	Boat	52.21	26.63
	Chair	51.61	73.37
 (14)	Boat A	58.70	0.01
	Boat B	53.13	91.76
	Chair	54.56	8.20
 (15)	Boat A	56.86	0.03
	Boat B	53.69	5.71
	Chair	52.03	94.26

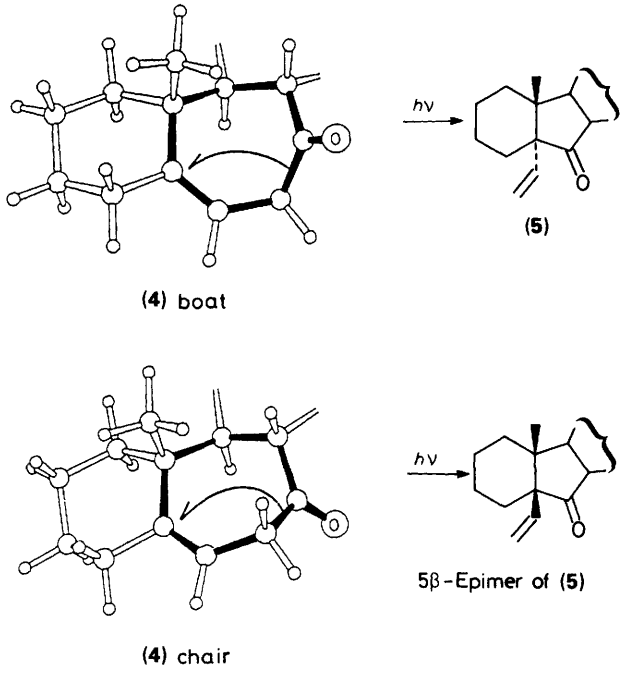
[a] Calculations were carried out at the computing centre of Hokkaido University. [b] Cholestane skeletons. [c] Ref. 6.

one (**4**) in t-butyl alcohol gives products arising from both [1,2] and [1,3] acyl migrations and that the vinyl ketone (**5**) and the cyclopropyl ketone (**6**) are formed from the excited singlet state and from the excited triplet state respectively. Intersystem crossing from the excited singlet to the triplet is thus more efficient in this 7a-homo-enone (**4**) than that in the 4a-homocholest-4a-en-3-one (**1**) where direct irradiation was reported to give only products arising from singlet [1,3] migrations.[4j]

In order to gain knowledge as to whether any correlation exists between the stereochemistry of the photo-products and the ground-state conformations of the starting β,γ-unsaturated ketones, ground-state conformer populations of the β,γ-unsaturated ketones (**1**), (**4**), and (**11**) as well as all the possible 4a-homocholestenones, 4a-homo-5α-cholest-4-en-2-one (**13**), 4a-homo-5α-cholest-3-en-1-one (**14**), and 4a-homo-5α-cholest-2-en-4a-one (**15**) were examined by means of empirical force-field calculations.[9]

The Table summarizes the results of the calculations (MM2)[9] of the relative energies of boat and chair conformations of all the five possible β,γ-unsaturated 4a-homocholestenones and the populations of each conformer. Figure 2 shows ORTEP[10] stereodrawings of the boat and chair conformations of these ketones. The Table indicates that the boat conformation (99.98%) of 7a-homocholest-5-en-7a-one (**4**)[6] is more stable than the chair while the chair conformation (99.23%) of 4a-homo-5α-cholest-1-en-4-one (**11**) is more stable than the boat.

Inspection of the ORTEP drawings of the boat and chair conformations of the β,γ-unsaturated ketone (**4**) suggests that if the photochemical [1,3] acyl shift takes place while the initial geometry of the carbon framework is maintained to give a kinetically controlled product, the boat conformation should give 5-vinyl-7-nor-5α-cholestan-6-one (**5**) whereas the chair conformation should give its 5β-isomer (Scheme 8). Similarly, the 1,3-acyl shift of the boat conformations of the β,γ-unsaturated ketone (**11**) should give 1α-vinyl-4-nor-5α-cholestan-2-one whereas the chair form should result in the formation of its 1β-epimer (**12**). Our above experiments confirmed that this is indeed the case; the β,γ-unsaturated ketone (**4**) which exists in the boat conformation gave exclusively the 7-norcholestanone (**5**) having a 5α-vinyl group while the β,γ-unsaturated ketone (**11**) which exists in the chair conformation gave the 4-norcholestenone (**12**) having a 1β-vinyl group. It should be noted that in both 1,3-acyl shifts, thermodynamically less stable epimers are the products.



Scheme 8.

The conformational dependence is again clear in the case of the photorearrangement of 4a-homocholest-4a-en-3-one (**1**) reported by Seeman and Ziffer.[4j] The Table indicates that the boat (30.8%) and the chair (69.2%) forms are in an equilibrium in this β,γ-unsaturated ketone (**1**). Inspection of the ORTEP drawing shows that a 1,3-acyl shift of the boat form will result in the 5α-vinyl ketone (**2**) while the chair form will give the 5β-epimer (**3**); the ratio of the 5α- to the 5β-isomer predicted by the ratio of the conformer populations is *ca.* 3:7. The reported yield of the 5β-isomer[3] is greater than that predicted from the calculated conformer populations. This deviation may be explained by assuming a secondary photochemical isomerization of part of the initially formed 5α-isomer to the 5β-isomer, as was indeed reported to take place.[4j]

Thus, there seems to be a clear dependence of the stereochemistry of the products arising from the 1,3-acyl shift on the ground-state populations of the conformers of the starting β,γ-unsaturated ketone in the [1,3] acyl photorearrangement of the three substrates (**1**), (**4**), and (**11**). This conformational specificity of the rearrangement clearly suggests the concerted or tight biradical nature of the [1,3] acyl shifts of these β,γ-

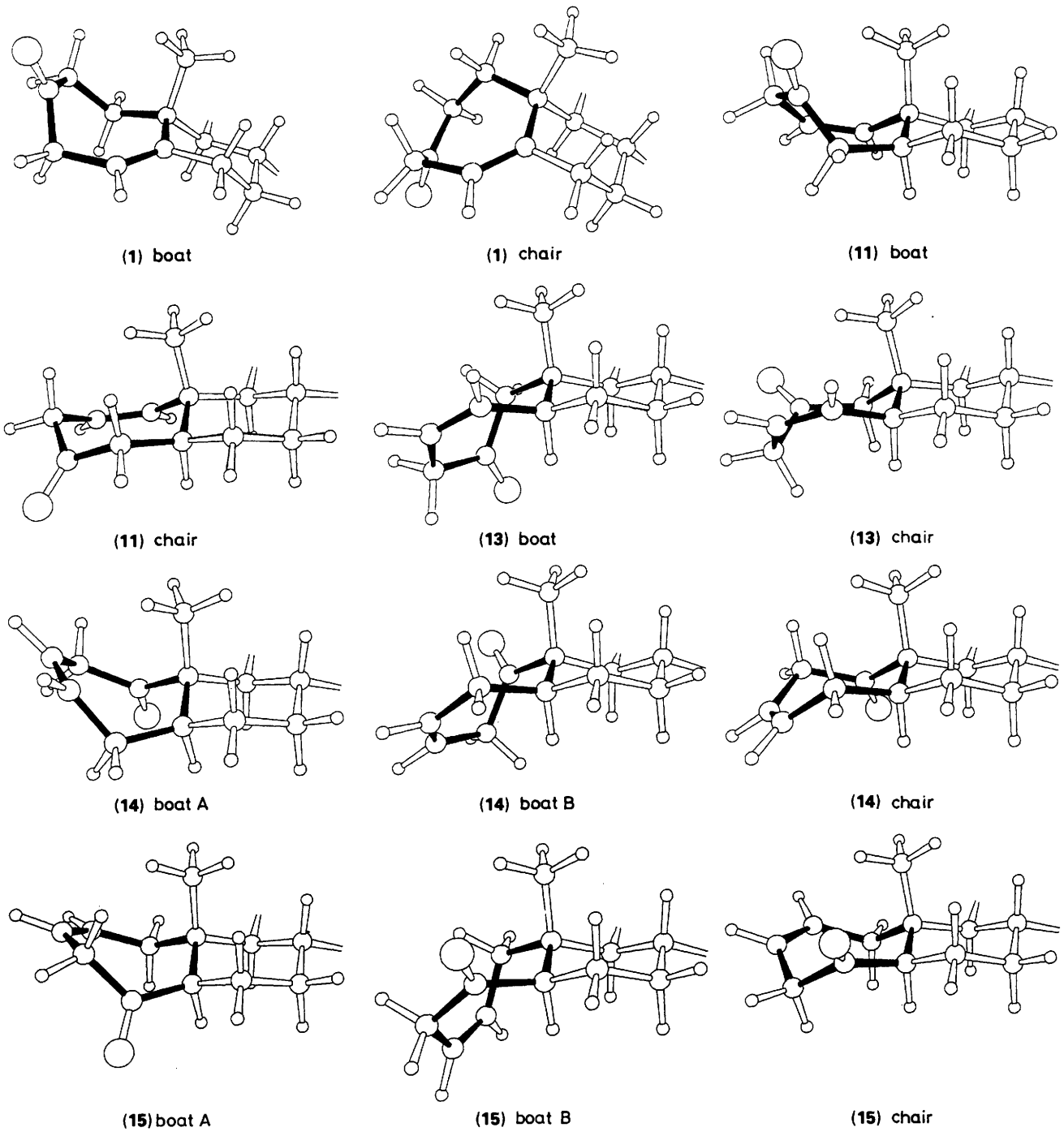


Figure 2. ORTEP drawings of the boat and chair forms of the β,γ-unsaturated ketones (**1**), (**11**), (**13**), (**14**), and (**15**). See Scheme 8 for drawings for (**4**).

unsaturated cyclic ketones which take place from their excited singlet states.[9]

More experiments on other substrates may prove the generality of our conclusions; the results will be the subject of future publications.

Experimental

M.p.s were determined with a Yanagimoto micro m.p. apparatus. IR spectra were determined for Nujol mulls with a Hitachi 260-10 spectrometer unless stated otherwise. ^{1}H NMR spectra were determined in $CDCl_3$ ($SiMe_4$ as internal reference) with a JEOL PS 100 high-resolution spectrometer (100 MHz) unless stated otherwise. High- and low-resolution mass spectra were recorded with a JEOL JMS-D 300 spectrometer (70 eV) by the staff of the Faculty of Agriculture or the microanalytical laboratory of the Faculty of Pharmaceutical Sciences of this university. ^{13}C NMR spectra were determined in $CDCl_3$ ($SiMe_4$ as internal reference) with a JEOL PS 100 high-resolution spectrometer. UV spectra were measured with a JASCO Ubest-30 UV/VIS spectrophotometer. ORD measurements were recorded with a JASCO J-20A instrument. TLC was

carried out on Merck silica gel 60-PF 254. t-Butyl alcohol was dried over calcium hydride or metallic sodium and distilled. Acetone used as a solvent was purified by fractional distillation. A mixture of *cis*- and *trans*-piperylene was distilled before it was used as a quencher in the photolysis.

7a-*Homocholest*-5-*en*-7a-*one* (**4**).—This β,γ-unsaturated ketone was prepared by the procedure described in the previous paper:[6] λ_{max}[tetrahydrofuran (THF)] 282 nm (ε 104); (Bu^{t}OH) 275 mm (ε 225).

Photolysis of 7a-*Homocholest*-5-*en*-7a-*one* (**4**) *in t-Butyl Alcohol.*—7a-Homocholest-5-en-7a-one (**4**) (259 mg) in dry t-butyl alcohol (70 ml) in a Pyrex vessel was flushed with nitrogen and photolysed in an atmosphere of nitrogen for 17 h with a 100 W high-pressure Hg arc. The solvent was removed under reduced pressure and examination of the product by TLC indicated the formation of two major products together with the starting ketone. Isolation of the products by preparative TLC gave 5-vinyl-7-nor-5α-cholestan-6-one (**5**) (77 mg, 30%) as the most mobile product; the starting ketone (22 mg, 8.5%) was eluted next, followed by the cyclopropyl ketone (**6**) (86 mg, 33%) as the least mobile component of the mixture. The *vinyl compound* (**5**) had m.p. 122–124 °C (from MeOH) (Found: C, 84.0; H, 11.5. $C_{28}H_{46}O$ requires C, 84.4; H, 11.6%); ν_{max} 1 730 (C=O) and 927 cm^{-1}; δ 6.26 (270 MHz) (1 H, dd, *J* 17.6 and 10.8 Hz, H_X), 5.00 (1 H, dd, *J* 1.1 and 17.6 Hz, H_A), and 5.18 (1 H, dd, *J* 1.1 and 10.8 Hz, H_B); λ_{max}(THF) 312 (ε 230); *m/z* 398 (M^+, 14.5), 150 (41.5), 135 (18.5), 122 (100), 107 (18.7), 93 (26.4), and 81 (18.7%). The cyclopropyl compound (**6**) had m.p. 109–111 °C (from MeOH) (Found: *m/z* 398.3572. $C_{28}H_{46}O$ requires *M* 398.3549); ν_{max} 1 668 (C=O), 863, and 760 cm^{-1}; δ($CDCl_3$) 0.67 (3 H, s, 18-H), 1.01 (3 H, s, 19-H), and 0.55 (1 H, s, cyclopropane H); *m/z* 398 (M^+, 27.6), 317 (29.4), 316 (26.8), 161 (14.8), 150 (57.6), 149 (19.7), 135 (29.0), 122 (100), 121 (31.6), 109 (21.7), 107 (30.7), 95 (33.9), 93 (33.9), 81 (33.3), and 55 (40.9%).

Reduction of the Cyclopropyl Ketone (**6**) *with Lithium and Liquid Ammonia.*—To liquid ammonia (25 ml) containing lithium (32 mg), the cyclopropyl ketone (**6**) (43 mg) in dry diethyl ether (20 ml) was added dropwise. The solution was stirred under reflux for 30 min and then cooled in dry ice, and the excess of lithium decomposed by the addition of ammonium chloride. After the removal of liquid ammonia, diethyl ether was added. The ethereal solution was washed with water and dried (Na_2SO_4). Usual work-up gave a mixture of products, preparative TLC of which gave the more mobile 5-methyl-5α-cholestan-7-one (**9**) (36 mg, 83%) and the less mobile dimer (**8**) (1.5 mg, 3%). The dimer (**8**) had m.p. 195–197 °C (from acetone–methanol) (Found: *M*, 798.7250. $C_{56}H_{94}O_2$ requires *M* 798.7250); ν_{max} 1 716 cm^{-1} (C=O); δ($CDCl_3$) 0.64 (6 H, 18- and 18′-H), 1.23 (3 H, s, 19-H), and 1.25 (3 H, s, 19′-H); *m/z* 798 (M^+, 8.4), 783 (M^+ − Me, 1.1), 780 (1.8), 765 (1.7), 414 (2.6), 386 (31.3), and 385 (100%).

The 7-one (**9**) had m.p. 73–75 °C (from acetone–methanol) (Found: *M*, 400.3689. $C_{28}H_{48}O$ requires *M* 400.3704); ν_{max} 1 717 cm^{-1} (C=O); δ($CDCl_3$) 0.64 (3 H, s, 18-H), 0.88 (3 H, s, 19-H), and 1.22 (3 H, s, 5α-Me); *m/z* 400 (M^+, 100), 385 (M^+ − Me, 6.0), 246 (31.5), 245 (32.7), 205 (19.7), 192 (42.2), 150 (19.6), 109 (33.2), 95 (24.5), and 55 (26.2%); ORD (THF) $[\alpha]_{450}$ −9.2°, $[\alpha]_{350}$ −30.3°, 'min' $[\alpha]_{313}$ −84.7°, 'max' $[\alpha]_{270}$ +41.2° (20 °C: *c* 0.000 59).

Photolysis of 7a-*Homocholest*-5-*en*-7a-*one* (**4**) *in Acetone.*—The ketone (**4**) (53 mg) in acetone (15 ml) in a Pyrex vessel was flushed with nitrogen and photolysed in an atmosphere of nitrogen for 16 h. Evaporation and TLC of the residue with benzene as eluant gave three fractions A, B, and C in order of mobility. Fraction A (13 mg, 25%) was the cyclopropyl ketone (**6**) and fraction B (9 mg, 17%) was the oily cycloadduct (**7**) arising from a Paterno–Büchi reaction; ν_{max}($CHCl_3$) 1 698 cm^{-1} (C=O); δ($CDCl_3$) 0.67 (3 H, s, 18-H), 0.99 (3 H, s, 19-H), 1.18, and 1.24 (each 3 H, s, *gem*-Me_2); *m/z* 456 (M^+, 1.0), 414 (44.7), 399 (28.4), 398 (M^+ − CH_3COCH_3, 36.9), 386 (23.5), 385 (44.2), 317 (32.4), 150 (60.2), 122 (85.2), 95 (89.0), 81 (81.5), 55 (100), and 43 (64.4%). Fraction C (13 mg) was an intractable mixture.

Photolysis of 7a-*Homocholest*-5-*en*-7a-*one* (**4**) *in t-Butyl Alcohol in the Presence of Piperylene.*—The ketone (**4**) (47 mg) in dry t-butyl alcohol (10 ml) containing piperylene (5 ml) was flushed with nitrogen and photolysed in an atmosphere of nitrogen for 18 h. TLC indicated a major spot due to 5-vinyl-7-nor-5α-cholestan-6-one (**5**). After evaporation of the solvent, the residue was subjected to preparative TLC with benzene–hexane (2:1) as eluant to give two fractions. The more mobile fraction (27 mg, 56%) was 5-vinyl-7-nor-5α-cholestan-6-one (**5**). The less mobile fraction (129 mg) was an intractable mixture of products including polymerized piperylene.

Photolysis of 5-*Vinyl*-7-*nor*-5α-*cholestan*-6-*one* (**5**).—The ketone (**5**) (55 mg) in acetone (25 ml) in a Pyrex vessel was flushed with nitrogen for 30 min and photolysed in an atmosphere of nitrogen for 20 h. Examination of the products by TLC indicated a major spot. Usual work-up of the solution gave a residue which was subjected to preparative TLC to give the product (**10**) (29 mg, 52%), which had m.p. 102–104 °C (from acetone–methanol) (Found: *M*, 398.3547, $C_{28}H_{46}O$ requires *M*, 398.3547); ν_{max} 1 681 cm^{-1} (C=O); δ($CDCl_3$) 0.63 (3 H, s, 18-H) and 1.06 (3 H, s, 19-H); *m/z* 398 (M^+, 41.7), 150 (75.2), 122 (100), and 55 (42.7%).

4a-*Homo*-5α-*cholest*-1-*en*-4-*one* (**11**).—This β,γ-unsaturated ketone was prepared according to the procedure reported elsewhere;[7] λ_{max}(Bu^{t}OH) 282 nm (ε 55).

Photolysis of 4a-*Homo*-5α-*cholest*-1-*en*-4-*one* (**11**) *in t-Butyl Alcohol.*—The ketone (**11**) (100 mg) in dry t-butyl alcohol (300 ml) in a Pyrex vessel was photolysed in an atmosphere of nitrogen for 3.5 h with a 450 W high-pressure Hg arc. The solvent was removed under reduced pressure to give the product which was dissolved in diethyl ether. The ethereal solution was washed with water, then with saturated brine, and dried (Na_2SO_4). Evaporation of the solvent gave an oily mixture of products; preparative TLC [silica gel; dichloromethane–benzene (2:1)] yielded five fractions: A (R_f 0.7; 4 mg), B (R_f 0.65; 10 mg), C (R_f 0.6; 34 mg), D (R_f 0.55; 9 mg), and E (R_f 0.3; 7 mg) in order of mobility. Fractions A, B, D, and E were intractable mixtures. Fraction C (34 mg, 34%) was 1β-vinyl-4-nor-5α-cholestan-2-one (**12**) [Found: *M*, (FI-MS) 398.3549. $C_{28}H_{46}O$ requires *M* 398.3547]; ν_{max}(neat) 1 746 (5 membered C=O), 985, and 915 cm^{-1}; δ(270 MHz) 0.65 (3 H, s, 19-H), 0.85 (3 H, s, 18-H), 2.26 (1 H, dd, *J* 18.69 and 7.33 Hz, 3β-H), 2.59 (1 H, d, *J* 8.79 Hz, 1α-H), 5.68 (1 H, ddd, *J* 17.2, 10.3, and 8.9 Hz, H_X), 5.17 (1 H, ddd, *J* 17.2, 1.8, and 0.73 Hz; H_A), and 5.31 (1 H, dd, *J* 10.3 and 1.8 Hz, H_B); *m/z* (FD-MS) 398 (M^+, 100%).

Determination of Quantum Yields.—The quantum yields were determined by photolysing solutions of the 7a-homoketone (**4**) (5 ml; 50 mg) and the appropriate quantity of piperylene in t-butyl in a merry-go-round apparatus for 2 h. Hexan-2-one dissolved in cyclohexane was used as an actinometer. The yields of the vinyl ketone (**5**) and the cyclopropyl ketone (**6**) were determined by HPLC (benzene as solvent) with 3-chlorocholest-5-ene as an internal standard and acetone was determined by VPC analysis.

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